

Beata Swieczko-Zurek

Gdańsk University of Technology, Department of Materials Science and Engineering,
Gdańsk, Poland

ENVIRONMENTAL DEGRADATION OF THE Cr-Mo STEELS IN LIQUID HYDROCARBONS

ABSTRACT

The susceptibility to stress corrosion cracking at tension at a strain rate 10^{-6}s^{-1} and under constant load, and to low cycle fatigue, was estimated for two alloy steels 26H2MF and 34HNM in boiler fuel and used mineral car engine oil. The observed effects were explained by hydrogen evolution, entry and interaction with dislocations.

Key words: alloy steels, hydrocarbons, hydrogen degradation

INTRODUCTION

Hydrogen may be absorbed by metals in many environments, even those containing no water [1-4]. The possibility of degradation of hydrocarbons and hydrogen entry from greases and oils was discussed in [5-13]. The presence of thin layer of hydrocarbons (grease) on the surfaces of iron and steels was observed to affect the internal friction, free oscillation frequency, mechanical properties and image of slip lines, in the temperature range 160-373 K, as observed also after hydrogen charging. The only explanation is decomposition of hydrocarbons on the steel surface and hydrogen absorption within the surface layer where hydrogen interacts with mobile dislocations. Degradation of steels in hydrocarbons and successive hydrogen intake were also suggested as a cause of sudden failure of heavy fuel separators, observed even after a few weeks in some ships [14,15]; improper heat treatment (no sufficient tempering) and was also suggested as due to, at least in part, hydrogen-enhanced fatigue cracking [15]. Despite those reports, no obvious evidence of hydrogen intake from hydrocarbons and hydrogen-enhanced decrease in mechanical properties has been confirmed so far. In another work [16] the hydrogen absorption and corrosion in hydrocarbons has been investigated. The present work has been aimed at determining whether in case of medium strength alloy steel, susceptible to hydrogen degradation [14], its exposure in hydrocarbons may really cause hydrogen-enhanced plasticity loss and/or brittle cracking. The test conditions and media have been selected in order to simulate operating conditions of fuel separators of ship engines and those for car engines.

EXPERIMENTAL

Two Polish alloy steels were tested: 26H2MF and 34HNM (two forgings). The chemical compositions of steels are shown in Tables 1 and 2.

The three different tests were performed: strain slow rate tests, constant load tests and low cycle fatigue tests.

The smooth cylindrical specimens (PN-EN ISO 7539-4), 4 mm in diameter and 40 mm of gauge length, were used in the slow strain rate and low cycle fatigue tests. The cylindrical specimens with the round notch (PN-EN 2832:2001) were prepared for constant load tests. The specimens were heat treated and then polished with abrasive papers, with the No. 1200 as the last.

Table 1. Chemical composition of the 26H2MF steel, wt. pct

Reference	C	Mn	Si	P _{max}	S _{max}	Cr	Ni _{max}	Cu _{max}	Mo	V
Acc. to PN-EN 10028-2	0.22÷0.3	0.3÷0.6	0.3÷0.5	0.035	0.035	1.5÷1.8	0.3	0.25	0.6÷0.8	0.2÷0.3
Analysis	0.30	0.431	0.45	0.007	0.0006	1.61	0.16	0.15	0.72	0.27

Table 2. Chemical composition of the 34HNM steel, wt. pct

Reference	C	Mn	Si	P _{max}	S _{max}	Cr	Ni	Cu _{max}	Mo	V _{max}
Acc. to PN-EN 10083-1+A1	0.32÷0.4	0.4÷0.7	0.17÷0.37	0.035	0.035	1.3÷1.7	1.3÷1.7	0.3	0.15÷0.25	0.05
Analysis (forging A)	0.33	0.54	0.29	0.001	0.003	1.4	1.41	0.25	0.165	0.008
Analysis (forging B)	0.27	0.37	0.21	0.003	0.02	1.53	1.50	0.34	0.15	0.007

The applied heat treatment parameters are shown in Table 3 and 4. The parameters were chosen from standards [15,16] in such a manner as to obtain possibly various microstructures.

Table 3. Heat treatment parameters of the 26H2MF steel

No. of heat treatment	Heat treatment operations	Temperature [°C]	Heating time [min]	Cooling medium
1	Normalizing	970	20	air
	Normalizing	940	20	air
	Tempering	700	120	air
2	Normalizing	970	20	Air
	Normalizing	940	20	air
	Quenching	880	20	oil
	Tempering	600	120	air

Table 4. Heat treatment parameters of the 34HNM steel

Forging	No. of heat treatment	Heat treatment operations	Temperature [°C]	Heating time [min]	Cooling medium
A	1	Normalizing	870	20	air
		Quenching	860	20	oil
		Tempering	680	120	oil
	2	Normalizing	870	20	air
	Quenching	860	20	oil	
	Tempering	560	120	oil	
B	3	Normalizing	970	20	air
		Normalizing	940	20	air
		Tempering	700	120	air

Three media were used in tests: used mineral oil (car engine oil), boiler fuel (component of ship fuels) and glycerin. All tests were made at temperatures corresponding to operation conditions: 80°C for used mineral oil and glycerin and 135°C for boiler fuel. Before any tests the specimens were immersed in test medium and exposed for 1,000 hrs at elevated temperature. Then the mechanical tests started without breaking the exposure.

The slow strain rate tests were made at a strain rate 10^{-6} s^{-1} . The following parameters were measured: tensile strength, relative elongation, reduction-in-area and fracture energy.

The constant load tests were performed on pre-notched specimens. They were subjected to loads of 0.90, 0.93 and 0.96 F_m for 34HNM steel and of 0.94, 0.96 and 0.98 F_m , where F_m - the maximum imposed force.

The fatigue tests were performed with the INSTRON 1195 tensile machine. The minimum elongation was 0 and maximum deformation 1,0 %, strain rate 10^{-2} s^{-1} . The relative elongation was used to The minimum following parameters were fixed and measured: the lowest and highest strain values (strain amplitude), strain rate, number of cycles and time to failure.

RESULTS

The slow strain rate tests showed no effect of the exposure in hydrocarbons on tensile strength and fracture energy value, within the limits of experimental error. The small change on elongation was observed, and noticeable – on reduction-in-area. The examples of last results are shown in Figs. 1-3.

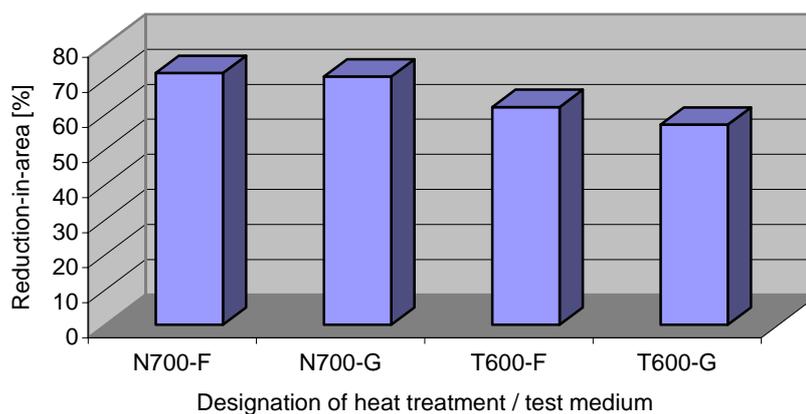


Fig. 1. Reduction-in-area of the 26H2MF steel subjected to different heat treatment (N700-No.1; T600-No.2) and tested in boiler fuel (F) or glycerin (G)

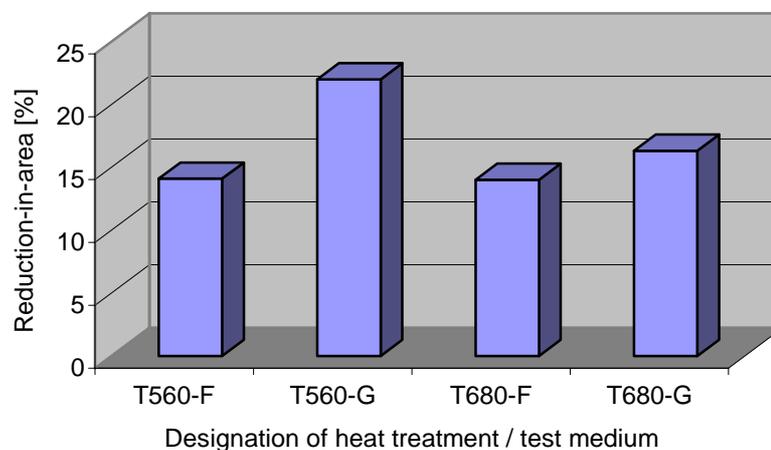


Fig. 2. Reduction-in-area of the 34HNM steel subjected to different heat treatment (T560 – No. 2; T680 – No. 1) and tested in boiler fuel (F) and glycerin (G)

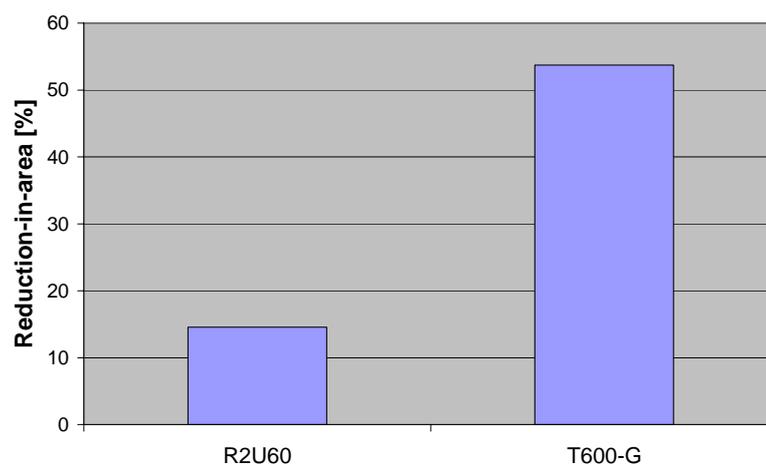


Fig. 3. Reduction-in-area of the 26H2MF steel subjected to quenching and tempering at 600°C, tested in used mineral oil (R2U60) and glycerin (G)

In constant load tests even at the highest load no failure during 200 h was observed. The low cycle fatigue tests were made only in boiler fuel and for the 34HNM steel subjected to heat treatment No. 3. The results are shown in Table 5. Each time the specimen exposed to boiler fuel failed after shorter time than that exposed to glycerin. Because of great differences in failure times, likely due to high sensitivity to the quality of surface preparation, the measured effects were evaluated by non-parametric statistical Wilcoxon and signs' tests. Upon the base of these tests, the time to failure in boiler fuel as comparing to that in inert medium was proved to be significantly shorter at high 0.99 confidence level.

Table 5. Results of low-cycle fatigue tests of the 34HNM steel subjected to different heat treatment, in boiler fuel and glycerin

Forging	Heat treatment	Environment	Number of cycles to failure
A	2	Boiler fuel	791
			2871
		Glycerin	17171
			16981
B	3	Boiler fuel	13911
			112701
		Glycerin	121541
			248731

DISCUSSION

In another work [15] the exposure of steels to hydrocarbons was shown to result in hydrogen absorption. The appearance of hydrogen might be caused by different processes: electrochemical corrosion in water phase under hydrogen control, chemical corrosion associated with presence of organic acids and/or decomposition of hydrocarbons with evolution of free hydrogen.

In liquid fuels the sulfur compounds, responsible of corrosive properties of hydrocarbons, are always present [17]. Besides, the fuels may contain some contaminants, water including. Water can be also absorbed from wet air, e.g. during long term storage in ship or harbor tanks. In oils also similar compounds may be found, and even organic and inorganic acids [18]. However, corrosion of steels observed in boiler and oil was shown to be relatively small and then it could not be the main process leading to hydrogen evolution [15].

The hydrogen source was the most likely so-called dehydrogenation reaction, i.e. cracking of long chains of hydrocarbons with an appearance of free atomic hydrogen. Such reaction occurs easily in presence of iron, being a catalytic agent, and at elevated temperature. The hydrogen intake absorption was facilitated by presence or formation in hydrocarbons of simple sulfur compounds.

Various effects of the exposure of steels in hydrocarbons observed in different tests may be explained by different stress - strain states.

In constant load tests in which no effects were observed, the maximum imposed force was below the yield strength and no plastic deformation occurred. In such conditions hydrogen cannot be effectively bound by a substantial number of structure defects. The

possibility of hydrogen delayed fracture is predicted by decohesion model of hydrogen embrittlement that is, according to these results, no applicable and the obtained results are then discussed within the framework of dislocation model.

At slow straining plastic deformation occurs after a short time and many cracks are initiated at different sites. The weak effects can be explained within the framework of dislocation model, according to which there is no sufficient amount of hydrogen to interact with a huge number of freshly formed dislocations.

In low cycle fatigue tests, well-known as the most susceptible technique of detection of environmental degradation, the single main crack is quickly formed. Then, hydrogen diffuses all the time to the tip of this main fatigue crack and may very effectively enhance its propagation.

CONCLUSIONS

The effects of exposure in hydrocarbons on mechanical properties observed in applied slow strain rate tests and low cycle tests may be attributed to decomposition of hydrocarbons at elevated temperature and hydrogen entry to the steels, the process facilitated by presence of sulphur compounds in fuels and oils.

The lack of effect of exposure in constant load tests, weak effect in slow strain rate tests and substantial effect in low cycle fatigue test may be explained upon the base of dislocation model of hydrogen embrittlement by different amount of hydrogen effectively trapped by different number of dislocations in various tests.

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REFERENCES

1. Hydrogen and corrosion degradation of metals. J. Flis [ed.], PWN, Warszawa, 1979.
2. Zielinski A., Cwiek J., Olive J.M.: Methods for characterizing hydrogen degradation of materials. *Advances in Materials Science* 3 (2002) pp. 5-11.
3. Zhang T.C., Jiang X.X., Li S.Z.: Hydrogen-induced embrittlement wear of a high-strength, low-alloy steel in an acidic environment. *Corrosion Science Section, NACE International*, 1997, pp. 200-205.
4. Ikeda A., Nakanishi M.: The resistance on cracking caused by hydrogen sulfide for gas pipings. *Sumitomo Search* No. 26 (1981), pp. 91-104.
5. Kula P., Pietrasik R., Wendler B., Jakubowski K.: The effect of hydrogen in lubricated frictional couples. *Wear* 212 (1997), pp. 199-205.

6. Kula P., Pietrasik R., Wendler B., Jakubowski K.: Hydrogen interaction in lubricated frictional nodes. *Tribologia*, No. 113 (1998), pp. 7-21.
7. Kula P., Pietrasik R.: The hydrogen influence of creation and exploitation of nitriding layers. *Inżynieria Materiałowa*, 21, 2000, pp. 114-120.
8. Kula P., Pietrasik R.: The hydrogen in surface layer and the friction. *Proc. XXIV Trib. School*, Krynica, 2000, pp. 425-437.
9. Kula P., Pietrasik R.: Hydrogen`s interaction with hardened surface layers in dry and lubricated frictional couples. *Inżynieria Materiałowa* 29 (1998), pp. 1085-1091.
10. Kula P., Pietrasik R.: The physicochemical influence of capacities surface layers on border friction. *Inżynieria Materiałowa* 30 (1999), pp. 546-549.
11. Kula P.: The comparison of resistance to „hydrogen wear” of hardened surface layers. *Wear* 178 (1994), pp. 117-121.
12. Łunarska E., Samatowicz D.: The hydrogen-induced modification of the properties of the metal surface coated with oil and lubricant. *Tribology International* 33 (2000) pp. 491-499.
13. Samatowicz D., Łunarska E.: Investigations of steel and iron covered with mineral oil by internal friction method. *Proc. 4th Int. Conf. Intermolecular Interactions in Matter*, Gdańsk, 1997, 36-41.
14. Michalak P., Kotkowski K. *et al.*: Hydrogen-enhanced fatigue of fuel installations in diesel engines. *Proc. Intl. Conf. Environm. Degrad. of Eng. Mat., EDEM 1999*, Gdansk, Poland, 1999, vol.1, pp. 346-350.
15. Świczko-Żurek B.: The estimation of 26H2MF and 34HNM alloy steels to degradation in technical liquid hydrocarbons. Ph. D. Thesis, Poznań University of Technology, 2005.
16. Świczko-Żurek B.: Corrosion and hydrogen intake for some Cr-Mn steels in liquid hydrocarbons. AMS, to be published.
17. Urbański P.: *The fuels and the lubricants*. WSM, Gdynia 1999
18. Podniało A.: *The fuels, oils and the lubricants in exploitation*. WNT, Warszawa 2002